

# Self-Consistent Field Calculations Using Two-Body Density Functionals for Correlation Energy Component: II. Small Molecules

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**ABSTRACT:** In part I of this series, self-consistent calculations using two-body density functionals for correlation energy were done and applied to atomic systems, giving very good results. We now apply the same scheme to small molecules. The examples studied include diatomic ( $\text{H}_2$ ,  $\text{Li}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{F}_2$ ,  $\text{HLi}$ ,  $\text{HBe}$ ,  $\text{HB}$ ,  $\text{HF}$ , and  $\text{HCl}$ ) as well as polyatomic ( $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}_2$ , and  $\text{O}_3$ ) molecules at their ground states. The values reported for equilibrium geometries, atomization energies, vibrational frequencies, and dipole moments are compared with experimental and other theoretical calculations, with good agreement in most cases. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 1899–1908, 1998

**Keywords:** Hartree–Fock exchange plus correlation functionals SCF calculations; two-body density; diatomics; polyatomics; equilibrium geometries; atomization energies; vibrational frequencies; dipole moments

## Introduction

In a previous study<sup>1</sup> we deduced new functionals for correlation energy from a modeling of the second-order reduced density matrix,  $\rho_2$ , based

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on the correlation factor approach. This consists of writing  $\rho_2$  as a product of a noncorrelated or partially correlated two-body density  $\rho_2^0$ , and a correlation factor,  $F$ , namely:

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = \rho_2^0(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) \cdot [1 + F(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)] \quad (1)$$

Following the processes detailed in ref. 1, a corrected Gaussian summation was used to approximate  $\rho_2^0$ , and two extensions to the Colle–Salvetti correlation factor were used for  $F$ . Additional re-

strictions, such as the virial theorem and the hierarchy between the two- and one-body densities, were imposed. When the reference  $\rho_0^2$  is chosen to be that provided by one Slater determinant, the final expression for the energy can be cast in the form:

$$E[\rho_\alpha^{det}, \rho_\beta^{det}] = E_{det}[\rho_\alpha^{det}, \rho_\beta^{det}] + E_c[\rho_\alpha^{det}, \rho_\beta^{det}] \quad (2)$$

with  $E_{det}$  being the energy provided by the Slater determinant, whereas  $E_c$  stands for the remaining correlation contribution.  $\rho_\alpha^{det}$  and  $\rho_\beta^{det}$  represent the  $\alpha$  and  $\beta$  components, respectively of the one-determinant charge density. The variational search for the minimum of  $E[\rho_\alpha, \rho_\beta]$  with respect to the orbitals that expand  $\rho_\alpha^{det}$  and  $\rho_\beta^{det}$  leads to pseudo-eigenvalue equations of the Kohn–Sham type, which can be solved to give the best estimates of  $E$ ,  $\rho_\alpha$ , and  $\rho_\beta$ .

In ref. 2, this scheme was applied to neutral atoms and their ions with  $Z$  ranging from 2 to 18. The ionization potentials, electron affinities, and average dipole polarizabilities were obtained for these systems. The results compared well with experimental data, and are of the same quality as the best results provided by other local and nonlocal exchange-correlation functionals.<sup>2</sup>

In this work we apply the same method of ref. 2 to the ground state of several molecules. Our purpose is to analyze the achievements and drawbacks of the functionals deduced in ref. 1 when they are applied to small molecules, rather than to carry out an extensive set of calculations over a wide range of molecular examples. Hence, we have selected systems that serve as typical test examples. For nonpolar molecules we selected the homonuclear diatomics  $H_2$ ,  $Li_2$ ,  $B_2$ ,  $C_2$ ,  $N_2$ ,  $O_2$ , and  $F_2$ . This set of molecules has been used extensively in test cases,<sup>3–8,11</sup> because it covers strongly bound systems such as  $N_2$ , weakly bound ones such as  $Li_2$ , and molecules with triplet as well as singlet ground states. For polar systems, the hydrides  $HLi$ ,  $HBe$ ,  $HB$ ,  $HF$ , and  $HCl$  provide a well-known series.<sup>5–9,12</sup>  $H_2O$  and  $NH_3$  are typical examples of small polyatomic molecules.<sup>10</sup> The conformation and energetics of  $H_2O_2$  are also typical problems for testing of correlation functionals.<sup>13</sup> Finally, the complex electronic structure of the ozone molecule<sup>14,15</sup> is an example of which high levels of theory are needed to obtain qualitatively good results.<sup>16</sup>

The properties that have been used for testing include binding energies ( $D_e$ ), equilibrium bond

lengths ( $R_e$ ), harmonic vibrational frequencies ( $\omega_e$ ), and electric dipole moments ( $\mu_e$ ) for diatomics. For polyatomics, we reported on atomization energies ( $E_{at}$ ), equilibrium geometries, and dipole moments. The effect of exchange and basis set dependence has been considered, and comparison with other correlation functionals has also been done.

In the next section, the details of the calculations are given. The third section is devoted to analysis of the results, and the concluding remarks are outlined in the final section.

## Calculations

In this section we give the results obtained for the molecules just mentioned, when solving the restricted-open-shell Kohn–Sham-type equations using the correlation potentials derived in ref. 2. The correlation energy functionals used in the calculations are the F1(6), F1(5), and F2(5) two-body functionals of ref. 2. F1(6) and F1(5) are the highest two levels of development for the F1 functional deduced in ref. 1, having five and four independent parameters, respectively, entering in their expressions. F2(5) is the highest level of development of functional F2 from ref. 1, which depends on four independent parameters. In addition to these functionals, we have performed calculations with the Vosko, Wilk, and Nusair<sup>17</sup> local functional (VWN), and with the nonlocal functional of Lee, Yang, and Parr<sup>18</sup> (LYP). The results obtained for the restricted-open-shell Hartree–Fock calculations are also given for comparison. All calculations were done using the Gaussian-92 suite of programs.<sup>19</sup>

A systematic study of the basis set effect in DFT calculations carried out on homonuclear diatomic molecules was done in another study.<sup>20</sup> The 6-311G\* provided very good performance when compared with double- or triple-zeta STO bases. To test the influence of still larger basis sets, we calculated the properties mentioned in the Introduction, using the F1(6) functional, together with the 6-311G\*\* and the more extended ANO-TZ,<sup>21,22</sup> for the whole set of molecules. The values obtained show no further improvement in the results and, hence, we report those of the 6-311G\*\* basis set.

The atomization energies have been calculated as the energy of the molecule at the optimized equilibrium geometry minus the energies of the atoms. The harmonic vibrational frequencies are obtained by numerical differentiation of the ana-

**TABLE I.**  
**Dissociation Energies (eV) for Several Diatomic Molecules in Their Ground States, Calculated Using Three Exchange Schemes.<sup>a</sup>**

	H <sub>2</sub>	Li <sub>2</sub>	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	LiH	BeH	HB	HF	HCl	mre <sup>b</sup>
Ex. <sup>c</sup>	4.75	1.14	3.00	6.36	9.91	5.21	1.66	2.52	2.20	3.58	6.12	4.62	
ROHF	3.62	0.17	0.86	0.65	4.96	1.10	−1.49	1.47	2.16	2.74	4.18	3.41	59.4
HF-F1(6)	4.67	1.70	2.86	4.51	10.44	5.68	3.12	2.70	2.73	3.99	5.70	5.05	20.5
HF-F2(5)	4.77	2.32	3.67	5.36	11.19	6.60	4.16	2.82	2.65	4.07	5.83	5.26	33.1
HF-F1(5)	4.57	1.44	2.17	3.62	9.50	4.32	1.39	2.61	2.80	3.92	5.59	4.76	15.9
HF-VWN	6.21	0.93	1.15	2.04	7.34	2.25	−0.89	3.30	3.30	4.38	5.95	5.02	44.1
HF-LYP	4.66	0.89	1.32	2.32	7.65	2.66	−0.57	2.43	2.51	3.60	5.30	4.37	32.3
B-F1(6)	4.75	1.70	4.47	8.07	13.14	8.98	5.92	2.78	2.67	3.99	6.32	5.18	45.5
B-F1(5)	4.65	1.45	3.79	7.19	12.19	7.60	4.16	2.68	2.73	3.91	6.19	4.88	27.9
B-VWN	6.28	0.93	2.77	5.62	10.04	5.53	1.88	3.35	3.22	4.37	6.55	5.14	17.5
B-LYP	4.74	0.90	2.94	5.90	10.34	5.90	2.16	2.51	2.45	3.61	5.90	4.50	8.1
BHH-F1(6)	4.70	1.70	3.59	6.17	11.68	7.20	4.36	2.73	2.69	3.97	5.98	5.10	28.8
BHH-F1(5)	4.60	1.44	2.91	5.28	10.74	5.83	2.61	2.63	2.75	3.90	5.86	4.81	14.5
BHH-VWN	6.24	0.92	1.89	3.71	8.58	3.76	0.33	3.31	3.25	4.36	6.22	5.06	30.2
BHH-LYP	4.69	0.88	2.06	3.99	8.89	4.15	0.64	2.46	2.47	3.59	5.57	4.42	17.8

<sup>a</sup>Hartree–Fock, Becke, and a 50% combination of the two, together with several correlation energy functionals (see text) with a 6-311-G\*\* basis set.

<sup>b</sup>Mean relative error over the whole set of molecules.

<sup>c</sup>In Tables I–III the exact values are taken from refs. 3 and 12, except for HCl, which are from ref. 24.

lytical first derivatives of the potential energy curve.

Table I provides the dissociation energies for the set of diatomic molecules mentioned in the Introduction. To analyze the role played by the exchange contribution, the calculations have been performed using the aforementioned correlation energy functionals, together with Hartree–Fock

(HF) exchange, Becke (B) exchange,<sup>23</sup> and a 50/50 mixing of the two (BHH). The corresponding equilibrium bond lengths are listed in Table II. The results for the harmonic vibrational frequencies and moduli of the electric dipole moments are given in Tables III and IV, respectively. Table V shows the results for the equilibrium geometries, atomization energies, and moduli of the electric

**TABLE II.**  
**Equilibrium Bond Lengths (Bohr) for Several Diatomic Molecules in Their Ground States.**

	H <sub>2</sub>	Li <sub>2</sub>	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	LiH	BeH	HB	HF	HCl	mre
Ex.	1.401	5.051	3.003	2.347	2.073	2.282	2.679	3.015	2.538	2.336	1.733	2.409	
ROHF	1.390	5.263	3.098	2.351	2.022	2.176	2.516	3.037	2.535	2.314	1.693	2.399	2.2
HF-F1(6)	1.383	5.160	3.071	2.338	2.016	2.168	2.502	3.007	2.520	2.297	1.687	2.384	2.2
HF-F2(5)	1.390	5.227	3.088	2.346	2.020	2.173	2.510	3.033	2.540	2.308	1.691	2.393	2.1
HF-F1(5)	1.377	5.156	3.054	2.328	2.012	2.163	2.493	2.989	2.502	2.281	1.682	2.375	2.5
HF-VWN	1.363	5.107	3.041	2.321	2.005	2.154	2.483	2.969	2.492	2.271	1.676	2.371	2.8
HF-LYP	1.379	5.100	3.042	2.324	2.008	2.156	2.479	2.976	2.503	2.284	1.682	2.380	2.5
B-F1(6)	1.419	5.188	3.094	2.397	2.104	2.349	2.770	3.057	2.567	2.371	1.766	2.617	2.6
B-F1(5)	1.412	5.183	3.076	2.386	2.098	2.339	2.757	3.038	2.545	2.353	1.760	2.446	1.6
B-VWN	1.398	5.126	3.065	2.380	2.091	2.329	2.745	3.014	2.535	2.341	1.752	2.443	1.1
B-LYP	1.414	5.130	3.065	2.381	2.093	2.328	2.732	3.023	2.546	2.356	1.759	2.451	1.3
BHH-F1(6)	1.399	5.163	3.077	2.363	2.054	2.240	2.613	3.028	2.541	2.329	1.722	2.415	1.0
BHH-F1(5)	1.393	5.159	3.059	2.353	2.049	2.233	2.603	3.010	2.521	2.312	1.716	2.406	1.2
BHH-VWN	1.379	5.106	3.047	2.346	2.042	2.224	2.592	2.988	2.511	2.301	1.709	2.402	1.4
BHH-LYP	1.395	5.104	3.048	2.348	2.044	2.225	2.584	2.995	2.523	2.315	1.715	2.411	1.1

TABLE III.  
Harmonic Vibrational Frequencies (cm<sup>-1</sup>) for Several Diatomic Molecules in Their Ground States.

	H <sub>2</sub>	Li <sub>2</sub>	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	LiH	BeH	HB	HF	HCl	mre
Ex.	4400	351	1051	1855	2358	1580	892	1406	2061	2368	4139	2991	
ROHF	4594	337	944	1911	2740	2030	1212	1431	2136	2476	4513	3148	10.5
HF-F1(6)	4647	357	975	1949	2767	2055	1236	1467	2162	2531	4562	3215	11.6
HF-F2(5)	4595	344	955	1927	2751	2039	1221	1436	2113	2496	4534	3176	10.7
HF-F1(5)	4689	357	993	1976	2788	2076	1253	1485	2200	2578	4604	3246	12.6
HF-VWN	4773	368	1006	1985	2804	2093	1263	1507	2218	2599	4637	3251	13.6
HF-LYP	4672	364	1006	1986	2797	2093	1277	1497	2192	2562	4597	3222	12.9
B-F1(6)	4308	327	960	1788	2290	1445	864	1353	1986	2219	3906	2829	5.0
B-F1(5)	4352	327	979	1814	2313	1468	876	1370	2032	2265	3952	2861	3.8
B-VWN	4436	336	988	1822	2331	1483	881	1397	2048	2289	3988	2865	2.8
B-LYP	4345	332	991	1827	2329	1490	903	1382	2023	2254	3956	2846	3.3
BHH-F1(6)	4492	345	975	1879	2555	1781	1056	1418	2083	2390	4267	3037	5.0
BHH-F1(5)	4534	345	993	1906	2577	1802	1070	1435	2125	2437	4312	3069	6.0
BHH-VWN	4615	355	1004	1915	2594	1819	1079	1459	2142	2461	4349	3073	6.6
BHH-LYP	4522	351	1006	1918	2588	1823	1096	1447	2114	2422	4313	3048	6.1

dipole moments of the polyatomic molecules mentioned in the Introduction. For comparison, available exact data are also listed in the tables. We have selected the values quoted in refs. 3 and 12 for  $R_e$ ,  $D_e$ , and  $\omega_e$  of the diatomics. The data for HCl are those of ref. 24. The exact dipole moments are those quoted in ref. 25, except for HBe, for which we give the value calculated by Meyer and Rosmus.<sup>26</sup>

TABLE IV.  
Moduli of Electric Dipole Moments (Debyes) for Several Diatomic Molecules in Their Ground States.

	LiH	BeH	HB	HF	HCl	mre
Ex. <sup>a</sup>	5.83	0.17	1.27	1.82	1.08	
ROHF	6.03	0.29	1.72	1.98	1.45	30.4
HF-F1(6)	6.03	0.27	1.74	1.98	1.44	28.2
HF-F2(5)	6.01	0.27	1.78	1.99	1.37	28.2
HF-F1(5)	6.02	0.27	1.76	1.98	1.43	28.4
HF-VWN	6.01	0.29	1.77	1.99	1.43	31.0
HF-LYP	5.93	0.28	1.76	1.99	1.47	30.0
B-F1(6)	5.71	0.29	1.36	1.85	1.37	23.4
B-F1(5)	5.70	0.30	1.39	1.85	1.36	23.3
B-VWN	5.72	0.31	1.41	1.86	1.37	24.8
B-LYP	5.59	0.30	1.39	1.86	1.40	24.4
BHH-F1(6)	5.91	0.28	1.57	1.93	1.41	25.3
BHH-F1(5)	5.90	0.28	1.59	1.93	1.41	25.5
BHH-VWN	5.90	0.30	1.61	1.93	1.41	28.2
BHH-LYP	5.80	0.29	1.59	1.94	1.44	27.2

<sup>a</sup>Exact values taken from ref. 25, except for HBe, whose value is that recommended in ref. 26.

For the experimental atomization energies of the polyatomic molecules we selected the values from ref. 27. The equilibrium geometries of H<sub>2</sub>O and NH<sub>3</sub> were taken from ref. 25. For H<sub>2</sub>O<sub>2</sub> the data were taken from ref. 30, and those for ozone from refs. 14 and 31. The ends of each of the rows of Tables I–IV show the mean relative errors obtained for each functional, calculated from the corresponding set of molecules.

Analysis of Results

The Hartree–Fock results without correlation are described thoroughly in ref. 25, and hence they are not investigated here. First, we examine the SCF results obtained by using the HF exchange, together with the correlation energy functionals. The second part of this section examines the effect of including the Becke exchange instead of HF. Finally, the results of using the BHH exchange scheme are also analyzed.

EXACT EXCHANGE

Atomization Energies

We can see from Tables I and V that all of the correlation energy functionals improve the Hartree–Fock atomization energies, with F1(6), F1(5), and F2(5) functionals giving better results, on average, than either VWN or LYP. Because

TABLE V.  
Atomization Energies (kcal / mol), Equilibrium Geometries (Bohr and Degrees), and Moduli of Electric Dipole Moments (Debye) for Some Polyatomic Molecules.<sup>a</sup>

Ex. <sup>b</sup>	ROHF	HF exchange				Becke exchange				1 / 2(HF + B) exchange						
		F1(6)	F2(5)	F1(5)	VWN	LYP	F1(6)	F1(5)	VWN	LYP	F1(6)	F1(5)	VWN	LYP		
H <sub>2</sub> O																
E <sub>at</sub>	234.5	155.1	226.7	232.3	221.9	237.4	207.1	246.9	241.6	257.0	227.0	235.6	230.6	246.1	216.0	
R <sub>HO</sub>	1.810	1.778	1.770	1.775	1.764	1.757	1.764	1.847	1.838	1.830	1.838	1.803	1.796	1.789	1.796	
HOH	104.5	105.5	105.6	105.5	105.7	105.9	105.8	102.7	102.9	103.1	103.0	104.4	104.6	104.8	104.7	
μ <sub>e</sub>	1.85	2.14	2.14	2.14	2.14	2.14	2.16	2.01	2.02	2.02	2.03	2.09	2.09	2.10	2.11	
NH <sub>3</sub>																
E <sub>at</sub>	300.9	198.4	307.7	315.9	300.7	323.4	277.6	327.4	319.9	342.5	297.0	316.4	309.2	331.8	286.2	
R <sub>NH</sub>	1.912	1.892	1.881	1.887	1.873	1.866	1.873	1.948	1.937	1.929	1.937	1.910	1.900	1.894	1.901	
HNH	106.7	111.4	111.7	111.5	111.1	110.9	111.0	113.4	113.2	112.9	113.0	112.1	111.9	111.7	111.7	
μ <sub>e</sub>	1.47	1.72	1.72	1.72	1.72	1.71	1.72	1.71	1.71	1.70	1.71	1.72	1.71	1.71	1.72	
H <sub>2</sub> O <sub>2</sub>																
E <sub>at</sub>	271.9	138.3	316.0	346.1	273.5	238.4	215.0	375.9	332.3	297.2	273.3	341.9	298.9	263.8	240.3	
R <sub>HO</sub>	1.824	1.780	1.771	1.777	1.765	1.760	1.767	1.853	1.845	1.839	1.847	1.806	1.799	1.794	1.801	
R <sub>OO</sub>	2.767	2.619	2.601	2.611	2.589	2.580	2.576	2.870	2.851	2.840	2.826	2.705	2.690	2.680	2.673	
HOH	99.4	102.7	102.8	102.7	103.0	103.0	103.1	98.4	98.6	98.7	98.8	101.1	101.3	101.4	101.4	
HOOH	111.8	116.4	116.1	116.3	116.0	116.1	115.9	123.2	122.9	123.1	122.3	118.8	118.6	118.7	118.4	
μ <sub>e</sub>	2.20	1.91	1.92	1.91	1.92	1.92	1.94	1.61	1.62	1.62	1.65	1.80	1.81	1.81	1.83	
O <sub>3</sub> C <sub>2v</sub>																
E <sub>at</sub>	148.8	-8.9	185.2	227.0	111.9	1.6	17.8	340.6	266.2	155.6	170.5	253.3	179.6	69.3	85.0	
R <sub>OO</sub>	2.404	2.257	2.246	2.253	2.239	2.232	2.231	2.471	2.459	2.449	2.445	2.331	2.322	2.314	2.312	
OOO	116.8	119.3	119.2	119.2	119.3	119.3	119.2	118.1	118.1	118.1	118.1	118.5	118.6	118.6	118.5	
μ <sub>e</sub>	0.53	0.87	0.87	0.87	0.87	0.87	0.87	0.54	0.55	0.55	0.55	0.71	0.71	0.71	0.71	
O <sub>3</sub> D <sub>3h</sub>																
E <sub>exc.</sub>	0.92	0.53	0.51	0.52	0.51	0.53	0.52	1.54	1.56	1.58	1.57	0.98	0.99	1.02	1.01	
R <sub>OO</sub>	2.740	2.561	2.545	2.555	2.536	2.528	2.527	2.809	2.793	2.784	2.776	2.650	2.638	2.629	2.627	

<sup>a</sup>The same procedures followed in Tables I-IV have been used here.  
<sup>b</sup>The values for the exact atomization energies are from ref. 27. The exact equilibrium geometries for water and ammonia are taken from ref. 25, those for H<sub>2</sub>O<sub>2</sub> from ref. 30, and those for O<sub>3</sub> from ref. 31. The excitation energy between the ground state of O<sub>3</sub>, X<sup>1</sup>A<sub>1</sub>C<sub>2v</sub>, and the <sup>1</sup>A<sub>1</sub>D<sub>3h</sub> excited state is from the accurate calculations of ref. 14. The moduli of the exact electric dipole moments are from ref. 25.

F1(6) and F2(5) give too-negative ground energies for the molecules, the corresponding atomization energies are generally overestimated by these functionals. This is not the case with F1(5), which provides very good estimates for both diatomic and polyatomic systems. On the other hand, LYP underestimates the atomization energies in almost every case (and this will be important when the Becke exchange is used instead of the exact one), whereas VWN overbinds the hydrides. There are two systems for which VWN and LYP give bad results, namely the  $F_2$  and  $O_3$  molecules. In the first case, the local minimum obtained with these two functionals lies *over* the energy of the separated atoms. This is due to the inability of these functionals to correct the Hartree–Fock potential energy curve, which is dissociative for this molecule.<sup>6</sup> On the other hand, the atomization energy of the ozone molecule is underestimated by these two functionals, giving an extremely weak bond.

Table VI shows the kinetic  $\Delta T$ , nuclei-electron  $\Delta V_{Ne}$ , classic coulomb  $\Delta J$ , exchange  $\Delta E_x$ , and correlation  $\Delta E_c$  contributions to the dissociation energy for the HBe, HF,  $C_2$ ,  $N_2$ ,  $O_2$ , and  $F_2$  molecules. The data include both exchange only or uncorrelated (ROHF and Becke), as well as correlated, results using the F1(5) [HF-F1(5), B-F1(5)] and LYP (HF-LYP, B-LYP) functionals. The well-known fact that good results can be obtained by adding the correlation energy to a SCF uncorrelated calculation<sup>6, 27–29, 32–34</sup> is also reflected in Table VI. Actually, good values of atomization energies can be obtained by adding the correlation contribution of the dissociation energy obtained in the correlated SCF calculation to the corresponding uncorrelated dissociation energy. This reflects the small contribution of the correlation potential to the effective one appearing in the pseudo-eigenvalue equations. This quasi-additivity of the correlation energy is responsible for the fact that changes between the results of SCF calculations, using different exchange schemes (e.g., HF vs. Becke) but the same correlation functional, are mainly due to exchange. The total electron–electron repulsion energy decreases with respect to the exchange-only results when the correlation energy is included in any of the correlation functionals. This is a consequence of the fact that they include the short-range correlation effects between electrons with different spin, thus not allowing the electrons to be near each other. The results listed in Table VI for the  $F_2$

molecule, using the LYP functional, show that the small atomization energies obtained with this functional are primarily concerned with the underestimation of the aforementioned correlation effects. The same is valid for the ozone molecule, and also for the VWN functional when applied to these two molecules. The  $O_3$  molecule is an example of a system in which accurate multideterminant calculations are needed to obtain results comparable with experiment.<sup>14–16</sup> This is reflected by the rather poor results obtained for the atomization energies of the ground state of ozone, and also for the excitation energy between this and the  $^1A_1$  ( $D_{3h}$ ) excited state, in comparison to results obtained for the rest of the molecules.

### Equilibrium Geometries

The nondynamical or long-range correlation effects are outside the scope of the calculations analyzed here. These effects are important when obtaining accurate potential energy curves for the molecules, and are related to the multiconfigurational character of the exact wave function.<sup>3, 12</sup> When a multiconfigurational calculation is performed, and a TBDF is added, the result is an increase in the equilibrium bond lengths, and a decrease in the vibrational frequencies, with respect to the Hartree–Fock values.<sup>3, 6, 12</sup> However, when only the short-range correlation effects are introduced via the correlation energy functionals, the overall effect is to move the charge to bonding regions of the molecule.<sup>36, 37</sup> This explains the shortening of the equilibrium bond lengths, with respect to the Hartree–Fock (or Becke alone) results. This fact can also be derived from Table VI, which reflects the increase in absolute value of both the nuclei-electron,  $\Delta V_{Ne}$ , and classic coulomb repulsion,  $\Delta J$ , contributions to the dissociation energy of the correlated calculations with respect to the exchange-only results associated with this charge redistribution. Because Hartree–Fock  $R_e$  ( $\omega_e$ ) values are normally shorter (larger) than experimental ones,<sup>25</sup> the values obtained for these properties when correlation is included through functionals of the density are even poorer than the Hartree–Fock ones. These findings are valid for both diatomic or polyatomic molecules. In the latter, shortening of equilibrium bond lengths is compensated for by a slight increase in the values of the equilibrium angles. As noted elsewhere,<sup>6</sup>

**TABLE VI.**  
**Energy Contributions (a.u.) to Atomization Energy of Some Diatomic Molecules.<sup>a</sup>**

	$R_e$	$\Delta T$	$\Delta V_{Ne}$	$\Delta J$	$\Delta E_x$	$\Delta E_c$
HBe						
ROHF	2.535	0.07759	−3.30458	1.67476	−0.10608	0
Becke	2.577	0.06649	−3.23059	1.62709	−0.09234 (−0.09676) <sup>b</sup>	0
HF-F1(5)	2.502	0.08603	−3.34882	1.69450	−0.10972	−0.02355
B-F1(5)	2.545	0.07544	−3.27491	1.64651	−0.09536	−0.02350
HF						
ROHF	1.693	0.19679	−11.31343	5.75444	−0.10775	0
Becke	1.760	0.22655	−10.90890	5.54838	−0.11358 (−0.13450)	0
HF-F1(5)	1.682	0.20920	−11.39691	5.79673	−0.11280	−0.05173
B-F1(5)	1.760	0.24013	−11.01579	5.60331	−0.11900	−0.05080
C <sub>2</sub>						
ROHF	2.351	−0.00868	−30.07576	14.65459	0.09473	0
Becke	2.411	0.08056	−29.78057	14.65565	−0.03970 (−0.06298)	0
HF-F1(5)	2.328	0.02624	−30.46922	14.86737	0.08499	−0.10929
B-F1(5)	2.386	0.11560	−30.17676	14.87194	−0.05060	−0.11024
N <sub>2</sub>						
ROHF	2.022	0.15519	−47.67132	23.05448	0.05158	0
Becke	2.112	0.21189	−46.08494	22.41915	−0.02735 (−0.08312)	0
HF-F1(5)	2.012	0.19532	−48.02565	23.24828	0.04048	−0.16685
B-F1(5)	2.098	0.25311	−46.48099	22.63285	−0.03886	−0.16614
O <sub>2</sub>						
ROHF	2.176	0.06505	−57.73093	28.20971	0.00326	0
Becke	2.362	0.13874	−53.69885	26.32337	−0.02512 (−0.10732)	0
HF-F1(5)	2.163	0.09270	−58.13754	28.36804	0.04233	−0.11824
B-F1(5)	2.339	0.16948	−54.25768	26.60242	−0.03473	−0.11641
F <sub>2</sub>						
ROHF	2.516	−0.03744	−63.48846	31.31795	0.06656	0
Becke	2.791	−0.00221	−57.55100	28.47210	0.01885 (−0.04953)	0
HF-F1(5)	2.493	−0.00620	−64.10182	31.62056	0.05668	−0.10569
B-F1(5)	2.757	0.02906	−58.32069	28.85020	0.01093	−0.10306
HF-LYP	2.479	0.28076	−64.43181	31.76935	0.05547	−0.03382
B-LYP	2.732	0.10515	−58.92594	29.11548	0.00526	−0.02305

<sup>a</sup>The results using only the Hartree–Fock exchange or Becke exchange are labeled ROHF and Becke, respectively. The entries labeled HF-F1(5) and B-F1(5) correspond to calculations including both exchange and correlation, with either Hartree–Fock (HF) or Becke (B) exchange functionals and F1(5) correlation energy functional. Results obtained using the LYP functional are also shown for the F<sub>2</sub> molecule.

<sup>b</sup>The values in parentheses correspond to the value of  $\Delta E_x^B$  evaluated at the ROHF equilibrium bond length.

shortening of the equilibrium distances is also responsible for the increase in harmonic vibrational frequencies of the diatomics, with respect to the Hartree–Fock results. Again, as the latter are usually above the exact results, the inclusion of a correlation energy functional in the Kohn–Sham–

like equations leads to even poorer results when compared with experimental ones. As mentioned earlier, to have the correct trends in bond lengths and vibration frequencies, a minimal multiconfiguration calculation, including the remaining correlation energy by a TBDF, is needed.<sup>35</sup>

## Electric Dipole Moments

The moduli of the Hartree–Fock dipole moments shown in Tables IV and V are greater than the experimental ones. This has been explained<sup>38</sup> as a consequence of the overestimation of the ionic contributions, compared with the covalent ones, by the Hartree–Fock wave function. On the other hand, the values of the electric dipole moments obtained with the correlation energy functionals are almost the same as the Hartree–Fock ones, and change very little with correlation functional employed. This is a consequence of the slight differences, on average, between the densities provided by both procedures, and also sheds light on the well-known fact that the electric dipole moment operator,  $\hat{\mathbf{p}} = -\sum_i \mathbf{r}_i$ , is a test of the accuracy of the first moment of the electron density.

## BECKE EXCHANGE

Here we consider the effect of using the Becke formula instead of the Hartree–Fock formula for exchange energy. Due to the relative weight of the correlation contribution just discussed, the differences between correlated SCF calculations using the Becke formula, with respect to those using HF exchange, are mainly due to the differing description of the exchange contribution and, to a much lesser extent, to the correlation component.

## Atomization Energies

Tables II and V show an increase in the atomization energies, with respect to the results obtained using the Hartree–Fock exchange—an exception being the HBe molecule. To better understand this result, we refer to Table VI, which shows that, except for HBe, the exchange contribution to the atomization energy,  $\Delta E_x$ , is always greater for the Becke than for Hartree–Fock exchange. Another important conclusion is that the Becke exchange moves charge toward the antibonding regions of the molecule, as shown by the smaller values of  $\Delta V_{Ne}$  and  $\Delta J$  contributions of the dissociation energy with respect to the Hartree–Fock values<sup>37</sup> (favoring larger equilibrium bond lengths), as has been noted previously.<sup>11,36</sup> Except for HBe, where the excess of exchange energy introduced by the Becke formula does not take place, the resulting energy balance gives larger dissociation energies. Actually, an empirical formula can be obtained that gives the difference between the Becke and Hartree–Fock

atomization energies using only the potential energy contributions, namely:

$$E_{at.}^B - E_{at.}^{HF} \approx -0.045N[\Delta V_B - \Delta V_{HF}] \quad (3)$$

where  $N$  is the number of electrons, and  $\Delta V = V_{NN} + \Delta V_{Ne} + \Delta J + \Delta E_x$  represents the difference between the molecular and separated-atom potential energy contributions. “B” stands for Becke and “HF” for Hartree–Fock values, respectively. The values (eV) of the approximated Becke atomization energies obtained with the above formula for HBe, HF, F<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, C<sub>2</sub>, and H<sub>2</sub>O are 2.09, 4.81, 1.28, 7.66, 4.85, 3.80, and 7.44, respectively, whereas the exact energies are 2.10, 4.82, 1.36, 7.68, 4.44, 4.20, and 7.64.

The overestimation of the Becke exchange contribution is especially significant for multiple-bonded molecules, such as C<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>, and also for small molecules containing lone-pair orbitals such as, for example, HF and F<sub>2</sub>. This seems to be due to the extra Fermi correlation introduced by Becke formula between like-spin electrons belonging to this kind of orbitals.<sup>39</sup> To verify this we calculated the difference between Becke and HF exchange contributions for the atomization energies ( $\Delta \Delta E_x = \Delta E_x^B - \Delta E_x^{HF}$ ) obtained for the above set of molecules at the Hartree–Fock equilibrium bond length (to avoid spurious geometrical contributions). The values obtained, divided by the bond order of each molecule, can be ordered, except for C<sub>2</sub>, by the number of like-spin pairs of valence electrons, namely  $-0.508$  (HBe:0),  $0.728$  (HF:4),  $1.222$  (N<sub>2</sub>:5),  $1.505$  (O<sub>2</sub>:6),  $2.145$  (C<sub>2</sub>:4), and  $3.159$  (F<sub>2</sub>:7).

This extra exchange contribution to the atomization energy introduced by the Becke formula tends to cancel the underestimation of correlation effects of the LYP functional, giving rather accurate results for both diatomic and polyatomic molecules. For the same reason, the remarkably good results obtained with the F1(5) functional are worsened by the same amount when the Becke exchange is used.

## Equilibrium Geometries and Dipole Moments

The extra repulsion between like-spin electrons introduced by the Becke exchange tends to separate them, with the aforementioned side-effect of moving charge to antibonding regions of the molecule.<sup>11,36</sup> Hence, the corresponding equilibrium bond lengths are larger than those obtained using the exact (Hartree–Fock) exchange. This, in



turn, explains the lowering of harmonic vibrational frequencies and the slightly smaller bond angles.

There are two opposite effects that the Becke exchange produces in the electric dipole moments. They can be realized using the well-known formula:

$$\mu = \sum_A^M Z_A \mathbf{r}_A - \int \mathbf{r} \rho(\mathbf{r}) d\mathbf{r} \quad (4)$$

where the first sum runs over the  $M$  nuclei in the molecule, each with charge  $Z_A$ , at position  $\mathbf{r}_A$ . As we have noted previously, the Becke exchange tends to give equilibrium bond distances larger than the Hartree–Fock exchange, thus increasing the first contribution in eq. (4). On the other hand, we have noted previously that, when the Becke exchange is used instead of the exact one, there is a net charge displacement to antibonding regions of the molecule. This second fact contributes to an increase in the second term in eq. (4), which counteracts the increase in nuclear contribution. The net effect is a lowering of the moduli of the dipole moments when compared with those obtained using exact exchange, for the whole set of molecules considered, except HBe.

As was pointed out when discussing the results obtained using the Hartree–Fock exchange, the equilibrium geometries, vibrational frequencies, and dipole moments do not depend so strongly on the type of functional employed, unlike the atomization energies do. Again, we find minor differences in the overall improvement on these properties among the correlation functionals employed when Becke exchange is used, with slightly better results for VWN.

## MIXING EXCHANGE

Using Becke exchange instead of Hartree–Fock exchange provides better estimates of  $R_e$ ,  $\omega_e$ , and dipole moments for every functional, although the cancellation of errors observed for the atomization energies occurs only for LYP and, to a lesser extent, also for VWN. On the other hand, the results obtained for this property by the F1(5) functional, together with the exact exchange, are very good. Hence, we have made calculations combining both types of exchange, using 50% of each, with the aim of seeing the capabilities of this functional when used in a simple hybrid exchange scheme. Tables I–V show the results obtained using this procedure, together with the values obtained using VWN and LYP functionals. The results for F1(5)

are better, on average, than those obtained using LYP or VWN.

## Concluding Remarks

The one-determinant SCF calculations using exact exchange and two-body functionals for correlation provide good results for the atomization energies for the molecules analyzed here, whereas density functionals, such as VWN and LYP, tend to underestimate the correlation energy of the molecule. This, combined with the overestimation of the exchange contribution when the Becke formula is used in the SCF procedure (mainly due to the extra Fermi correlation between electrons in different bonding or lone-pair orbitals) explains the improvement in the LYP and VWN results for the atomization energies, and the worsening obtained with the two-body functionals.

The shortening of the bond length, for the correlated SCF calculations, with respect to the ROHF values, common to every correlation functional, is due to the charge displacement over the bonding regions of the molecule, and is also the cause for the larger harmonic vibrational frequencies obtained when correlation is included in the calculations. On the contrary, when the Becke exchange is used in the SCF equations, the equilibrium bond lengths are larger, as a consequence of the charge displacement over antibonding regions of the molecule, with the corresponding lowering of the harmonic vibrational frequencies. These effects alter the modulus of the dipole moments, with the net effect of lowering its value when compared with the SCF calculations using exact exchange.

The results obtained combining 50% exact (Hartree–Fock type) and 50% Becke exchange give intermediate values between those obtained with each exchange type, with the best results provided by the F1(5) functional. However, this is only a check of the capabilities of the F1(5) functional, and we must remember that the ultimate reason for this improvement is based on a cancellation of errors. A better way to obtain chemical accuracy results would be to incorporate the multideterminant character right from the beginning. This can be accomplished by our two-body functionals because they depend on the two-body density of the reference wave function. Although we have performed calculations adding the correlation correction *a posteriori* to a GVB calculation,<sup>6,40</sup> it would be better to incorporate this through the GVB

variational search. This kind of procedure is currently being developed by our group.<sup>41</sup>

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